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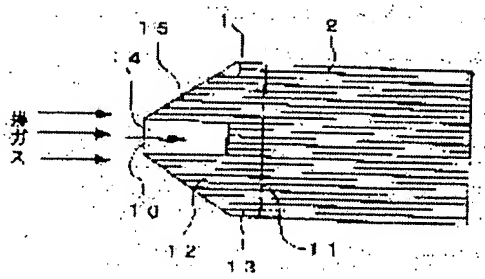
## (54) DEVICE FOR CLEANING EXHAUST GAS AND CATALYTIC CARRIER USED FOR THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To shorten such time that an exhaust gas-cleaning catalyst arranged on the downstream side of an HC adsorption member is raised to activation temperature.

SOLUTION: In the device for cleaning exhaust gas, an HC adsorption member 1 is arranged on the upstream side of the flow path of exhaust gas and an exhaust gas-purifying catalyst 2 is arranged on the downstream side thereof. The end face of the HC adsorption member 1 opposed to exhaust gas flow is formed into a truncated cone shape and also a hole part 14, which is opened in the end face and extended into the inner part of a honeycomb base material, is formed. A comparatively large part of exhaust gas reaching the ed face on the upstream side of the HC adsorption member 1 pass through the hole part 14 and therefor exhaust gas rapidly reaches the exhaust gas leaning catalyst 2 and the temperature of the same is rapidly raised.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the catalyst support used for the exhaust gas purge arranged on the emission way of an automobile, and its exhaust gas purge.
[0002]
[Description of the Prior Art] In connection with emission control in recent years, various kinds of catalyst equipments are arranged on the emission way of an automobile. For example, an oxidation catalyst oxidizes and purifies HC and CO in exhaust gas by the catalysis of the noble metals currently supported. Moreover, a three way component catalyst is NOx by the HC and CO while it oxidizes and the catalysis of the noble metals currently supported purifies HC and CO in the exhaust gas of a SUTOIKI ambient atmosphere. It returns and purifies. Furthermore, it is NOx. An occlusion reduction type catalyst is NOx while oxidizing HC and CO in a hyperoxia ambient atmosphere. NOx which carried out occlusion and was emitted in the SUTOIKI - fuel rich ambient atmosphere It returns and purifies.
[0003] For example, the three way component catalyst is designed so that the exhaust gas of the SUTOIKI ambient atmosphere which burned in theoretical air fuel ratio may be purified efficiently. However, the time of city area transit, and in sudden acceleration or sudden moderation, since an air-fuel ratio is changed focusing on SUTOIKI, the exhaust gas ambient atmosphere may be widely changed from HC rich ambient atmosphere to HC lean atmosphere, and it may become inadequate purifying it by the three way component catalyst. Moreover, HC is not purified but has the fault of being discharged as it is until the temperature of exhaust gas is low at the time starting or between the colds and exhaust gas temperature turns into more than the activation temperature of a catalyst.
[0004] The exhaust gas purge which has arranged HC adsorption members, such as a zeolite, to the upstream of a three way component catalyst is developed as indicated by JP,6-154538,A etc. there. In this exhaust gas purge, it ****s at the time of a temperature up, and oxidation purification of the HC by which HC in exhaust gas was made to stick to HC adsorption member at the time of low temperature, and was adsorbed is carried out by the three way component catalyst. Therefore, according to such an exhaust gas purge, since discharge is controlled since HC adsorption member is adsorbed, and oxidation purification is carried out with a three way component catalyst at the time of an elevated temperature, HC contained in exhaust gas at the time of starting between the colds etc. can control discharge of HC from low temperature to an elevated temperature.
[0005] As for this exhaust gas purge, it is common to consider as the structure of the tandem die which has arranged HC adsorption member of a honeycomb configuration to the upstream of an emission way, and has arranged the three way component catalyst of a honeycomb configuration to that downstream. And HC adsorption member and a three way component catalyst form few clearances in being arranged in the condition that there is no clearance, are put in order, or prepare spacing greatly, are put in order, and are used.
[0006]
[Problem(s) to be Solved by the Invention] In the exhaust gas purge of the tandem die which has arranged HC adsorption member of a honeycomb configuration to the upstream of an emission way, and has arranged the three way component catalyst of for example, a honeycomb configuration to the downstream, since HC adsorption member adsorbs HC efficiently even if it is exhaust gas of temperature lower than the activation temperature of three way component catalysts, such as the time of starting, it becomes possible to control discharge of HC.
[0007] However, since the heat of exhaust gas was taken by HC adsorption member of the upstream, the temperature up of the three way component catalyst of the downstream was delayed by such exhaust gas purge, and there was fault that non-purified exhaust gas would be discharged by the time a three way component catalyst serves

as activation temperature.
[0008] As for the catalyst support used for the further conventional HC adsorption member, three way component catalyst, etc., the honeycomb support of the shape of an abbreviation cartridge of cross-section regularity is used. Therefore, active principles with which the velocity distribution of the exhaust gas which flows support is supported by these since [ with the largest axis section ] the periphery section becomes small, such as HC adsorption material and noble metals, had the fault that use effectiveness was low, in the periphery section, although the axis section was used efficiently.
[0009] Then, the catalyst for which the end section countered emission in nothing and its conic end section, and has arranged the cone configuration is also known. If the catalyst of such a configuration is used, the velocity distribution of the exhaust gas which flows the inside of a catalyst can be made uniform, and the use effectiveness of active principles, such as HC adsorption material and noble metals, will improve.
[0010] However, when the end section uses for HC adsorption member of the exhaust gas purge of the tandem die which described above the support which makes a cone configuration, since the heat of exhaust gas gets across to the whole HC adsorption member at homogeneity, the heating value taken by HC adsorption member increases further, and there is a problem that temperature ups, such as a three way component catalyst of the downstream, are delayed increasingly.
[0011] This invention is made in view of such a situation, and the emission-gas-purification catalyst arranged at the downstream of HC adsorption member aims at shortening the time amount which carries out a temperature up to activation temperature.
[0012]
[Means for Solving the Problem] The description of the exhaust gas purge of this invention which solves the above-mentioned technical problem It is the exhaust gas purge which comes to arrange the emission-gas-purification catalyst which has arranged HC adsorption member which adsorbs the hydrocarbon in exhaust gas at the upstream of an emission way, and supported noble metals to the downstream of HC adsorption member. It is in HC adsorption member consisting of a base material which makes a honeycomb configuration with two or more honeycomb paths, and HC adsorption material covered by the base material, carrying out opening to the end face which counters emission, being prolonged inside a base material, and having the pore of a bigger path than the path of a honeycomb path.
[0013] Moreover, the description of the catalyst support of this invention which solves the above-mentioned technical problem is approximately cylindrical catalyst support which makes a honeycomb configuration with two or more honeycomb paths which extend in shaft orientations, and the end section which counters emission and is arranged has it in an outer diameter carrying out opening of the **** configuration which becomes large to the end-face center section of nothing and the end section, being prolonged toward the downstream, and having the pore of a bigger path than the path of a honeycomb path toward the downstream.
[0014]
[Embodiment of the Invention] In the exhaust gas purge of this invention, HC adsorption member which carries out opening to the front face which counters emission, is prolonged inside a base material, and has the pore of a bigger path than the path of a honeycomb path is arranged to the upstream of an emission way, and the emission-gas-purification catalyst is arranged at the downstream. Therefore, as for the exhaust gas which arrived at the upstream side edge side of HC adsorption member, comparatively many of the parts pass a pore, and since the ventilation resistance of a pore is smaller than a honeycomb path, exhaust gas reaches the emission-gas-purification catalyst of the downstream promptly. Moreover, in order that the exhaust gas which flows an emission way may have the velocity distribution that the rate of flow is large and the rate of flow is as small as the periphery section as a core and the big core of the rate of flow may advance into a pore, the time amount which reaches the emission-gas-purification catalyst of the downstream compared with the exhaust gas which flowed into the periphery section is shortened further. The surface area of the wall surface of a pore is still smaller than the sum total area of the wall surface of two or more honeycomb paths which made sum total opening area the same.
[0015] Therefore, the heating value of exhaust gas which flowed into the pore taken compared with the exhaust gas which flowed into the honeycomb path of the periphery section decreases, and hot exhaust gas reaches the end face of the emission-gas-purification catalyst of the downstream. Since time amount until the temperature up of the temperature of the emission-gas-purification catalyst of the downstream is carried out at an early stage and it turns into activation temperature by this can be shortened, the rate of purification improves.
[0016] As for the upstream edge which counters the emission of HC adsorption member, it is desirable to make the **** configuration to which an outer diameter becomes large toward the downstream. Since the velocity distribution

of the exhaust gas which flows the inside of HC adsorption member by this becomes uniform except for a pore, HC can be adsorbed efficiently and the amount of adsorption equivalent to the conventional HC adsorption member without a pore can be secured. Therefore, the discharge of HC in a low-temperature region can be reduced further. Moreover, since the whole is heated by homogeneity, HC adsorption member is effective in local degradation being prevented.

[0017] And toward the downstream, in the catalyst support of this invention, the end section which counters emission and is arranged carries out opening of the **** configuration to which an outer diameter becomes large to the end-face center section of nothing and the end section, is prolonged toward the downstream, and has the pore of a bigger path than the path of a honeycomb path by it. Therefore, with having described above, heating up times, such as an emission-gas-purification catalyst arranged at that downstream, are shortened according to the same operation, and the use effectiveness of the active principle supported by the support of a parenthesis improves.

[0018] As for the opening area of a pore, it is desirable that it is 1 - 40% of the cross section of HC adsorption member or the other end of catalyst support. If the opening area of a pore becomes smaller than this range, since ventilation resistance will go up and a difference with a honeycomb path will become small, it is hard coming to obtain the effectiveness which prepared the pore. Moreover, if the opening area of a pore becomes larger than this range, HC amount of adsorption of HC adsorption member which the number of honeycomb paths decreases and is said to this invention will fall, and the use effectiveness of the active principle currently supported by the catalyst support of this invention will fall.

[0019] This pore may penetrate the base material, and it can also constitute it as it extends to the middle of a base material and there to the downstream end face serves as a honeycomb path. Although HC amount of adsorption increases so that it is short, since HC amount of adsorption decreases although the heating up time of the emission-gas-purification catalyst of the downstream is shortened so that the die length of a pore is lengthened, and the compaction effectiveness of the heating up time of the emission-gas-purification catalyst of the downstream becomes small, the die length of a pore is determined according to a quality design. And it becomes possible to reconcile reservation of HC amount of adsorption, and compaction of a heating up time by this. Moreover, as a pore is a base material, it can prevent that the configuration prolonged [ to ], then hot exhaust gas contact the emission-gas-purification catalyst of the downstream directly, and degradation of the emission-gas-purification catalyst of the downstream can be controlled.

[0020] The rate of the exhaust gas which furthermore advances into the pore to the amount of the whole exhaust gas is so large that an engine speed is low, and it is so clear that an engine speed becomes high that its flow equalizes. Therefore, at the time of the low-speed rotations at the time of an idle etc., since exhaust gas advances into a pore efficiently, the temperature up of the emission-gas-purification catalyst of the downstream can be carried out at an early stage, and at the time of high-speed rotation, since hot exhaust gas flows HC adsorption member to homogeneity mostly, although it has the pore, it can control degradation of the emission-gas-purification catalyst of the downstream further.

[0021] In addition, especially as for the cross-section configuration of a pore, a triangle, a square, a round shape, etc. are not restricted. Moreover, it is good for the direction in which a pore is prolonged also as cross-section regularity, and the cross section can also consider as the configuration which narrows gradually, or the configuration which spreads gradually.

[0022] The configuration at the time of making the upstream edge of HC adsorption member into a **** configuration and the **** configuration of the edge of the upstream of catalyst support can be made into a 6[ a triangular pyramid, a square drill, and ] -sided pyramid, a cone, etc. Moreover, it is good also as a triangular pyramid base, a truncated four-sided pyramid, a truncated cone, etc. And the drill configuration may be continuously prolonged to the edge of the downstream, even the middle from an upstream edge to a downstream edge can be made into a drill configuration, and the remainder can also be made into the configuration of the triangle pole, the square pole, a cylinder, etc. Moreover, it is good as structure where the honeycomb path was formed in the interior by making a periphery front face into a drill configuration, and an inner circumference front face can also be made into the shape of a typeface of cross-section **** as a drill configuration.

[0023] HC adsorption member is formed from the base material which makes a honeycomb configuration, and HC adsorption material covered by the base material. A ceramic or metal, such as cordierite, etc. are illustrated as the quality of the material of a base material. The same is said of the quality of the material of the catalyst support of this invention. Moreover, as HC adsorption material, zeolites, such as a ferrierite, ZSM-5, mordenite, and Y mold zeolite, can be used. Moreover, it is also desirable to make into HC adsorption material what supported noble metals, such as palladium and silver, to the zeolite. Thus, by supporting noble metals, adsorbent [ of HC of low

molecular weight ] improves further. Although this HC adsorption material can be united with a base material by carrying out a wet coat to the front face of said base material, and calcinating on it, it can also form a base material from HC adsorption material depending on the case.

[0024] It is not restricted especially as an emission-gas-purification catalyst arranged at the downstream of HC adsorption member, but they are an oxidation catalyst, a three way component catalyst, and NOx. An occlusion reduction type catalyst etc. is illustrated. Depending on the case, two or more HC adsorption members may be arranged to a serial. Moreover, HC adsorption member and an emission-gas-purification catalyst may separate and arrange spacing, and may arrange it in the condition that there is no spacing. In the case of the latter, it is also possible to form HC adsorption member and an emission-gas-purification catalyst from the support base material of one.

[0025] For example, if it explains in the case of a typical three way component catalyst, the same three way component catalyst as the former which consists of porosity oxide support and noble metals supported by porosity oxide support can be used. As porosity oxide support, it can choose from an alumina, a silica, a silica alumina, a zirconia, a titania, etc., and can use. Especially the gamma-alumina that was excellent in an adsorption property and thermal resistance especially is desirable.

[0026] Moreover, to the above-mentioned porosity oxide support, it is desirable to support or mix oxygen occlusion emission material, such as the Seria and Seria-zirconia. The oxygen density in exhaust gas can be stabilized by this oxygen occlusion emission material, and since it is stabilized further and exhaust gas can be made into a SUTOIKI ambient atmosphere, the purification activity of a three way component catalyst improves further.

[0027] As noble metals supported by the above-mentioned porosity oxide support, a kind or two or more sorts can be chosen and used from platinum (Pt), a rhodium (Rh), palladium (Pd), iridium (Ir), etc. The amount of support of these noble metals receives 1l. of porosity oxide support. It is desirable to be referred to as 0.1-10g. It becomes expensive, while effectiveness will be saturated even if purification activity runs short and it supports mostly from this if fewer than this.

[0028] A three way component catalyst can be used as a pellet configuration or a honeycomb configuration. When considering as a honeycomb configuration, a coat layer can be formed in the honeycomb support base material formed from cordierite or a metallic foil from porosity oxide support, and it can manufacture by making the coat layer support noble metals. Or noble metals may be beforehand supported to porosity oxide support powder, and a coat layer may be formed and manufactured from the noble-metals support support powder.

[0029] In the emission-gas-purification catalyst arranged at the downstream, it is desirable to support many noble metals locally in the center section of the upstream end face. Since it is the part where the center section of the upstream end face is on extension of a pore, and a programming rate becomes large most, ignition is promptly performed by supporting many noble metals into the part, and efficient purification is attained also in low-temperature exhaust gas because it spreads for the whole catalyst.

[0030] Moreover, it can use for the above-mentioned HC adsorption member, and also the catalyst support of this invention can be used as support of the conventional emission-gas-purification catalysts, such as an oxidation catalyst and a three way component catalyst. And other catalysts of the downstream can shorten the time amount which carries out a temperature up to activation temperature by arranging the acquired catalyst to the upstream of an emission way, and arranging other catalysts to the downstream.

[0031]

[Example] Hereafter, an example and the example of a trial explain this invention concretely.

[0032] (Example 1) The exhaust gas purge of one example of this invention is shown in drawing 1 and drawing 2 . This exhaust gas purge consists of an HC adsorption member 1 arranged at the upstream of an emission way, and a three way component catalyst 2 arranged at the downstream of HC adsorption member 1.

[0033] The path of 30mm and the major-axis side edge side 11 HC adsorption member 1 103mm, the truncated-cone section 12 with a height of 21mm, and the path of a cross section It consists of 103mm and the cylinder section 13 with a die length of 27mm, and is capacity. It is 300 cc. [ the minor-axis side edge side 10 ] The minor-axis side edge side 10 is arranged at the upstream, emission is countered, and the major-axis side edge side 11 is continuing, without opening spacing in a three way component catalyst 2. And the pore 14 with a diameter of 20mm carries out opening in the center of the minor-axis side edge side 10, and a pore 14 is prolonged in the height direction (shaft orientations) of HC adsorption member 1, and is formed in die length of 38mm. Moreover, one side which carries out opening to HC adsorption member 1 in the minor-axis side edge side 10 and the major-axis side edge side 11 The countless honeycomb path 15 of 1.2mm angle is formed in homogeneity.

[0034] For this HC adsorption member 1, it consists of a honeycomb base material made from cordierite, and ZSM-

5 layer which was calcinated behind the wet coat and formed in the honeycomb base material front face, and ZSM-5 layer is per 1l. of honeycomb base materials. 200g is formed.

[0035] Moreover, a three way component catalyst 2 is nothing and its path about the shape of a cylindrical shape of cross-section regularity. 103mm, die length 120mm and capacity are 1000 cc. This three way component catalyst 2 consists of a gamma-alumina layer which was calcinated behind the wet coat and formed in the honeycomb base material and honeycomb base material front face made from cordierite, and Pt supported by the gamma-alumina layer. A gamma-alumina layer is per 1l. of honeycomb base materials. 200g is formed and 1g per 1l. of honeycomb base materials of Pt(s) is supported.

[0036] (Example of a comparison) The path of a cross section It considered as 103mm and the shape of a cylindrical shape with a die length of 35mm, and the exhaust gas purge of the example of a comparison was constituted using the same three way component catalyst as an example 1 using the same HC adsorption member as an example 1 except not having a pore 14.

[0037] (A trial and evaluation)

<Example 1 of a trial> These exhaust gas purges are arranged to evaluation equipment, respectively, the model gas of a SUTOIKI ambient atmosphere is entered, and it is gas temperature. HC, CO, and NOx at the time of making it circulate on condition that 400 degrees C and space-velocity 100,000h-1 The rate of purification was measured with elapsed time. The result of the exhaust gas purge of an example 1 is shown in drawing 3 , and the result of the exhaust gas purge of the example of a comparison is shown in drawing 4 .

[0038] As for the exhaust gas purge of an example 1, drawing 3 and drawing 4 show that the rate of purification very high to the inside of a short time is shown, and activity is high at an early stage compared with the example of a comparison. It is clear that its it is the effectiveness by having used the configuration as the triangular pyramid base while this forms a pore 14 in the upstream end face of HC adsorption member 1.

[0039] The model gas of a SUTOIKI ambient atmosphere is entered about the exhaust gas purge of the <example 2 of trial> example 1, and the example of a comparison, and it is gas temperature. On 900 degrees C and the conditions of space-velocity 100,000h-1 The durability test passed for 300 hours was performed. And it is from a room temperature with a sink at the conditions of space-velocity 100,000h-1 about the model gas same about each equipment durability test before and after a durability test. The temperature up was carried out to 400 degrees C, and the rate of HC purification in each temperature was measured. Each HC50% purification temperature is computed from the obtained data, and a result is shown in drawing 5 .

[0040] Drawing 5 shows that degradation extent by the durability test is smaller than the example of a comparison in the exhaust gas purge of an example 1. This is the effectiveness by having used the configuration as the truncated cone, and is considered that the temperature of the exhaust gas which flows into a three way component catalyst 2 was equalized, and local degradation was controlled by considering as a truncated-cone configuration while it forms a pore 14 in the upstream end face of HC adsorption member 1.

[0041] Various paths of the pore 14 of HC adsorption member 1 used in the <example 3 of a trial>, next the example 1 were changed, and various HC adsorption members were produced. In addition, the die length of the cylinder section 13 is adjusted and it was made for the volume of HC adsorption member to become fixed. And an exhaust gas purge is formed like the example 1 of a trial, respectively, the model gas of a SUTOIKI ambient atmosphere is entered, and it is gas temperature. It was made to circulate on condition that 400 degrees C and space-velocity 100,000h-1, and the temperature of the upstream end-face center section of the three way component catalyst 2 15 seconds after circulation initiation was measured. The relation between the path of a pore 14 and the measured temperature is collectively shown in drawing 6 .

[0042] From drawing 6 , the temperature of a three way component catalyst 2 is high in the range whose path of a pore 14 is 10-40mm, and the path of a pore 14 is understood that the range of 10-40mm is the optimal.

[0043] Out of HC adsorption member produced in the example 3 of the <example 4 of trial> trial, the path of a pore 14 chose what is 10mm, 20mm, and 30mm, and equipped the emission way of an automobile engine, respectively. And the velocity distribution around HC adsorption member when raising an engine speed from idle rotation to 4000 rpm is measured, respectively, and a result is shown in drawing 7 as rate-of-flow deflection to an engine speed.

[0044] From drawing 7 , in low-speed rotation, it was not concerned with the path of a pore 14, but the rate-of-flow deflection is greatly separated from 1, but the rate-of-flow deflection is approaching 1, so that it becomes high-speed rotation. Moreover, the rate-of-flow deflection is so close to 1 that the path of a pore 14 is small. This means that the inflow rate to a pore 14 decreased and the whole equalized as exhaust gas flows into a pore 14 at the time of low-speed rotation and it becomes high-speed rotation.

[0045] That is, by forming a pore 14, the rate of the exhaust gas which flows into a pore 14 at the time of low-speed

rotation is high, and it becomes homogeneity, so that it becomes high-speed rotation. Therefore, at the time of the low-speed rotations at the time of an idle etc., since exhaust gas advances into a pore efficiently, the temperature up of the catalyst of the downstream can be carried out at an early stage, and at the time of high-speed rotation, since hot exhaust gas flows HC adsorption member to homogeneity mostly, although it has the pore, it can control local degradation of the catalyst of the downstream.

[0046] in addition, as shown in drawing 8 , the pore 14 other than the exhaust gas purge shown in the example 1 penetrates HC adsorption member 1 -- as -- you may constitute -- moreover, the configuration of a pore 14 -- a cross section -- as it does not restrict uniformly and is shown in drawing 9 , it can also consider as a cone configuration. If it does in this way, since a travelling direction is regulated further, the exhaust gas which advanced into the pore 14 can heat a three way component catalyst 2 still more nearly locally.

[0047] Moreover, as shown in drawing 10, space 16 can also be formed between three way component catalysts 2 as HC adsorption member 1' of the shape of a typeface of cross-section ****. If it does in this way, since exhaust gas will serve as a turbulent flow in space 16, the end face of a three way component catalyst 2 can be heated to homogeneity in the large range, and local degradation can be prevented.

[0048]

[Effect of the Invention] That is, according to the exhaust gas purge of this invention, the catalyst of the downstream can shorten the time amount by which a temperature up is carried out to activation temperature, and the rate of purification can be raised further. Moreover, since degradation of the catalyst of the downstream can be controlled, the purification engine performance stabilized for a long period of time is obtained.

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[Translation done.]